Preparation and Diels–Alder Reactivity of Benzothieno[2,3-*c*]- and Benzothieno[3,2-*c*]-pyran-3-ones, Benzothiophene-2,3-quinodimethane Analogues; Synthesis of Dibenzothiophenes

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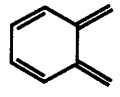
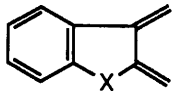
The benzothieno[2,3-*c*]pyran-3-ones (**6**) and the isomeric [3,2-*c*]pyranones (**7**) are stable analogues of benzothiophene-2,3-quinodimethane (**3**). When heated with alkynes they undergo Diels-Alder reactions to give, after loss of carbon dioxide, dibenzothiophenes. The regiochemistry of the Diels–Alder reaction is discussed.

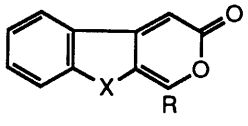
ortho-Quinodimethane (**1**) has found wide application as a reactive intermediate in organic synthesis,[1] but with the exception of indole-2,3-quinodimethane (**2**), the heterocyclic analogues of (**1**) have been less widely studied. However the synthetic potential of heterocyclic quinodimethanes as useful dienes has been amply demonstrated in the indole series by the intramolecular Diels–Alder reactions of (**2**) used by Magnus and co-workers,[2] and by work on stable cyclic analogues such as the pyrano[3,4-*b*]indole-3-ones (**4**) and the isomeric pyrano[4,3-*b*]indol-3-ones (**5**) developed in our own laboratories.[3–9] In view of the recent interest in benzothiophene-2,3-quinodimethane (**3**), a reactive intermediate generated by flash vacuum pyrolysis of 2-chloromethyl-3-methylbenzothiophene,[10] or by reaction of 2,3-bis(bromomethyl)benzothiophene with sodium iodide,[11] we decided to investigate the preparation of, and the Diels–Alder reactions of the benzothienopyranones (**6**) and (**7**), and we now report our results in full.[12] Interestingly, 1-phenylbenzothieno[2,3-*c*]pyran-3-one (**6**; R=Ph) has been prepared before, although only one Diels–Alder reaction of it was reported.[13]



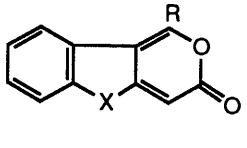
(**1**)



(**2**) X = NR
(**3**) X = S



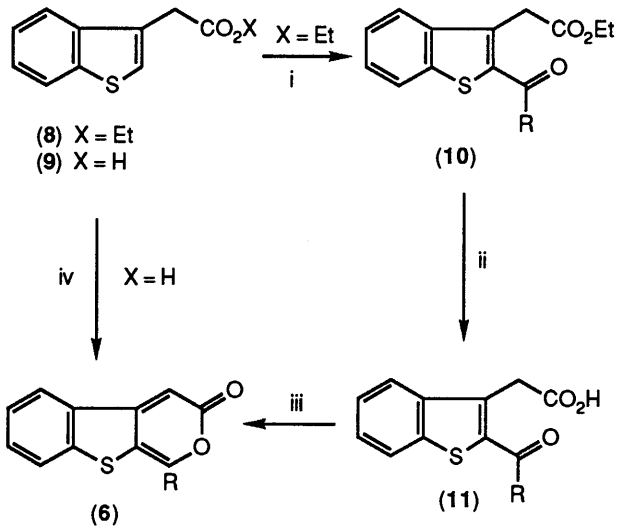
(**4**) X = NH
(**6**) X = S



(**5**) X = NH
(**7**) X = S

Results and Discussion

Preparation and Diels–Alder Reactions of Benzothieno[2,3-c]-*pyran-3-ones.*—The benzothieno[2,3-*c*]pyran-3-one ring system (**6**) was prepared by two methods, either starting from ethyl benzothiophen-3-ylacetate (**8**) or the corresponding acid (**9**).[14] The first method, which was needed to prepare the unsubstituted pyranone (**6a**), involved acylation of the ester (**8**) with dichloromethyl methyl ether or acetyl chloride in the presence of tin(IV) chloride to give the 2-formyl (**10a**) or 2-acetyl (**10b**) compounds respectively. Hydrolysis of the esters (**10**) gave the corresponding acids (**11**) which cyclised when heated in acetic anhydride to give the pyranones (**6a**) and (**6b**) in good yield. The pyranone (**6b**) and the pentyl substituted compound (**6c**) could also be prepared from benzothiophen-3-ylacetic acid (**9**) by reaction with the appropriate carboxylic acid anhydride in the presence of boron trifluoride–diethyl ether, exactly as for the corresponding indoles.[3–7]



Scheme 1. (**a**, R=H; **b**, R=Me; **c**, R=C_5H_{11}). *Reagents:* i, Cl_2CHOMe (or AcCl), $SnCl_4$, CH_2Cl_2; ii, KOH, H_2O, THF, MeOH; iii, Ac_2O, reflux; iv, $(RCO)_2O$, $BF_3 \cdot Et_2O$.

The benzothieno[2,3-*c*]pyran-3-ones (**6**) are yellow crystalline solids, which exhibit the expected spectroscopic properties. For example, the carbonyl frequencies in the IR spectra occur in the range 1 690–1 710 cm^{-1}, and the signal for 4-H on the pyranone rings is in the range δ 6.6–6.8 in their ^1H NMR spectra. For comparison, the corresponding indole derived pyranones (**4**) have IR carbonyl frequencies at *ca.* 1 690 cm^{-1}, and 4-H resonates at *ca.* δ 6.5.[5]

When heated with alkynes in boiling bromobenzene, the benzothieno[2,3-*c*]pyran-3-ones (**6**) undergo Diels–Alder reaction to give, after loss of carbon dioxide, dibenzothiophenes (Table 1). The reactions with the electron-deficient alkyne, dimethyl acetylenedicarboxylate (DMAD), proceeded quickest (Entries 1,4, and 10) and gave the dibenzothiophene-2,3-diesters (**12a, d, j**) in good to excellent yields. The reactions of the corresponding indole dienes (**4**) with DMAD also gave good yields of products, although they were over in a shorter time.[5]

The Diels–Alder reactions of the benzothienopyranones (**6**)

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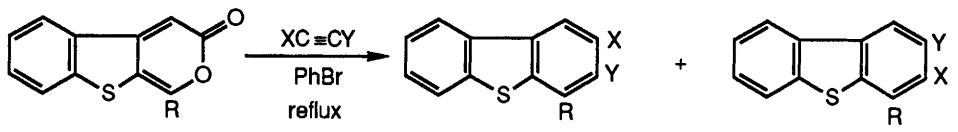
Table 1. Diels–Alder reactions of benzothieno[2,3-*c*]pyran-3-ones (**6**) with alkynes.



(6) (12) (13)

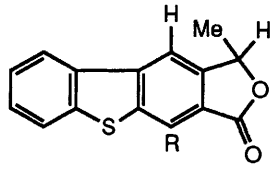
Entry	R	X	Y	Time (h)	(12)/(13)	Combined yield (%)	Ratio (12):(13)
1	H	CO_2Me	CO_2Me	5	**a**	79	—
2	H	H	CO_2Et	36	**b**	65	1:1
3	H	$SiMe_3$	CO_2Et	36	**c**	69	6:1
4	Me	CO_2Me	CO_2Me	8	**d**	93	—
5	Me	H	CO_2Et	24	**e**	79	1.5:1
6	Me	$SiMe_3$	CO_2Et	70	**f**	67	>20:1[a]
7	Me	MeCH(OH)	CO_2Me	80	**g**	46	>20:1[a,b]
8	Me	Me	CO_2Me	168	**h**	59	5:1
9	Me	Ph	CO_2Me	144	**i**	70	1.2:1
10	C_5H_{11}	CO_2Me	CO_2Me	14	**j**	68	—
11	C_5H_{11}	H	CO_2Et	36	**k**	54	1:1
12	C_5H_{11}	$SiMe_3$	CO_2Et	168	**l**	60	>20:1[a]
13	C_5H_{11}	MeCH(OH)	CO_2Me	192	**m**	55	>20:1[a,b]
14	C_5H_{11}	Me	CO_2Me	264	**n**	34	6:1
15	C_5H_{11}	Ph	CO_2Me	264	**o**	70	1.6:1

[a] Only a single product observed by 270 MHz ^1H NMR. [b] Initial product cyclises to the lactone (**14**)—see text.

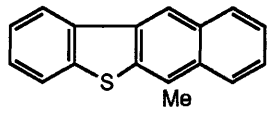
with other alkynes exhibit varying degrees of regioselectivity. Ethyl propiolate (Entries 2, 5, and 11) gives essentially equal amounts of the dibenzothiophene 2-(**12**) and 3-esters (**13**), with, in one case, a slight preference for the formation of the 2-ester (**12e**). These results are similar to those obtained with the indole pyranones (**4**) which, in the absence of steric factors, also exhibit little regioselectivity in their reactions with ethyl propiolate,[5] and confirm the view that propiolic esters, in contrast to other alkynes, are essentially unselective in their Diels–Alder reactions with 2-pyrones.[15] Similarly, methyl phenylpropiolate (Entries 9 and 15) exhibited only a small amount of regioselectivity, although methyl tetrolate (Entries 8 and 14) was somewhat more selective in its Diels–Alder reaction. However, ethyl trimethylsilylpropynoate, in which the acetylenic hydrogen is replaced by the bulky trimethylsilyl group, is highly regioselective in its Diels–Alder reactions with the benzothienopyranones (**6**) (Entries 3, 6, and 12) and gives the corresponding 3-trimethylsilyldibenzothiophene 2-esters (**12c, f, l**) in good yield.

The structure of the dibenzothiophene (**12f**) was confirmed by nuclear Overhauser effect (NOE) difference spectroscopy, in which pre-irradiation of the singlet at δ 0.38 ($SiMe_3$) caused enhancement of the singlet at δ 8.23 (4-H), and *vice versa*. Protodesilylation of (**12f**) with aqueous trifluoroacetic acid gave ethyl 1-methyldibenzothiophene-2-carboxylate (**12e**), identical with the major product obtained from the reaction of the benzothienopyranone (**6b**) with ethyl propiolate. The Diels–Alder reactions of the benzothienopyranones (**6b, c**) with methyl 4-hydroxypent-2-ynoate (Entries 7 and 13) were also highly regioselective, although the initial product, the dibenzothiophenes (**12g**) and (**12m**) could not be isolated, cyclising to the lactones (**14**) under the reaction conditions. The structure of the lactone (**14a**) was confirmed by NOE difference spectroscopy, in which pre-irradiation of the singlet at δ 7.98 due to 10-H caused enhancements of the signals at 5.63 (quartet, 1-H), and 1.67 (doublet, 1-Me), and 8.22 (double doublet, 9-H). No effects were observed on pre-irradiation of the singlet due to the 4-Me group at δ 2.96.

The benzothienopyranone (**6b**) also reacted with benzyne.



(**14**) **a** R = Me; **b** R = C_5H_{11}



(**15**)

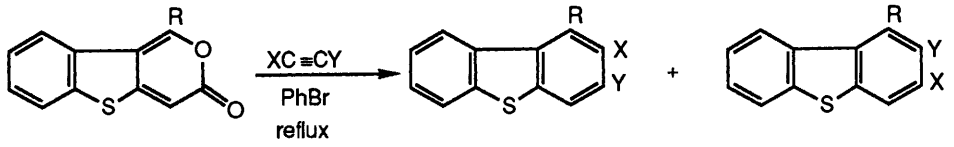
Thus the pyranone when heated with the benzyne precursor, 2-(3,3-dimethyltriazen-1-yl)benzoic acid, in boiling bromobenzene for 12 h gave the benzo-fused derivative (**15**) in 39% yield.

Thus the benzothieno[2,3-*c*]pyran-3-ones (**6**) undergo Diels–Alder reactions with alkynes to give dibenzothiophenes in good yield. With the exception of ethyl propiolate, the regiochemistry of the cycloaddition is the same as that observed with the corresponding indole derived dienes (**4**).

Preparation and Diels–Alder Reactions of Benzothieno[3,2-c]*pyran*-3-*ones*.—The isomeric benzothieno[3,2-*c*]pyran-3-ones (**7**) were prepared from ethyl benzothiophen-2-ylacetate (**16a**) or the corresponding acid (**16b**).[16] The ester (**16a**) could be formylated or acetylated at the 3-position using dichloromethyl methyl ether or acetyl chloride in the presence of tin(IV) chloride to give the corresponding 3-acyl compounds (**17**) in 76 and 46% yield respectively (Scheme 2). Hydrolysis of the ester (**17**) proved difficult, and the corresponding acids (**18**) could never be obtained pure. Nevertheless the impure formyl acid (**18a**) could be cyclised to the parent benzothienopyranone (**7a**) [42% from ester (**17a**)]. The 1-methylbenzothienopyranone (**7b**) could be prepared from the acid (**16b**) in 58% yield by reaction with acetic anhydride in the presence of boron trifluoride–diethyl ether (Scheme 2).

These benzothieno[3,2-*c*]pyran-3-ones are yellow–orange solids with the expected spectroscopic characteristics (carbonyl absorptions at *ca.* 1 705 cm^{-1} in their IR spectra, and peaks at *ca.* δ 6.48 for 4-H in their NMR spectra), and exhibit similar Diels–Alder reactivity to the [2,3-*c*]-isomers (**6**). Thus when

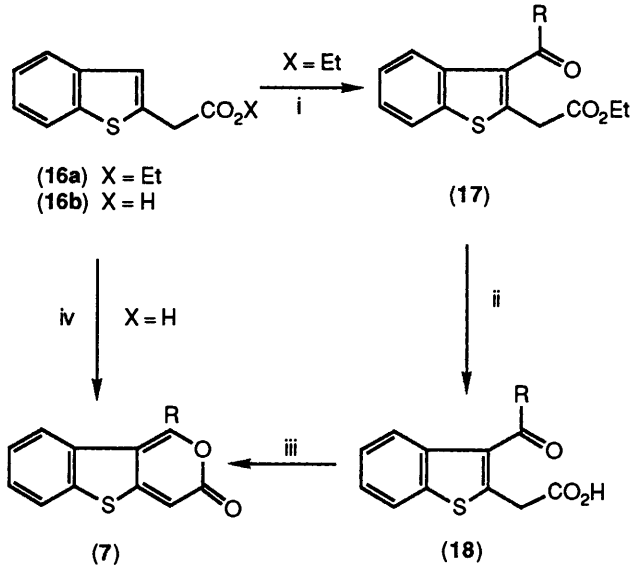
Table 2. Diels–Alder reactions of benzothieno[2,3-*c*]pyran-3-ones (**7**) with alkynes.



(**7**) (**19**) (**20**)

Entry	R	X	Y	Time (h)	(19)/(20)	Combined yield (%)	Ratio (19):(20)
1	H	CO_2Me	CO_2Me	7	**a**	73	—
2	H	H	CO_2Et	24	**b**	74	1:1.6
3	H	$SiMe_3$	CO_2Et	24	**c**	78	1:10
4	Me	CO_2Me	CO_2Me	9	**d**	73	—
5	Me	H	CO_2Et	40	**e**	76	1:1.9
6	Me	$SiMe_3$	CO_2Et	192	**f**	31	1 : >20[a]
7	Me	Me	CO_2Me	192	**g**	35	1:10
8	Me	Ph	CO_2Me	192	**h**	66	1:3

[a] Only a single product observed by 270 MHz ^1H NMR.



Scheme 2. (**a**, R=H; **b**, R=Me). *Reagents:* i, Cl_2CHOMe (or AcCl), $SnCl_4$, CH_2Cl_2; ii, KOH, H_2O, THF, MeOH; iii, Ac_2O, reflux; iv, Ac_2O, $BF_3 \cdot Et_2O$.

heated with DMAD in boiling bromobenzene they give the dibenzothiophene diesters in good yield (Table 2, Entries 1 and 4). Although the reactions with ethyl propiolate and methyl phenylpropiolate (Entries 2, 5, and 8) exhibit very little regioselectivity, as before the corresponding reactions of methyl tetrolate and ethyl trimethylsilylpropynoate (Entries 3, 6, and 7) were more selective, with the silylated alkyne being highly regioselective. The direction of addition, however, is, perhaps not surprisingly, opposite to that of the isomeric dienes (**6**), a feature which parallels the chemistry of the related indole dienes (**4**) and (**5**).[5,8]

Conclusions.—The isomeric benzothienopyranones (**6**) and (**7**), easily prepared from benzothiophene-2- or -3-ylacetic acid, are stable benzothiophene-2,3-quinodimethane type dienes, which react with alkynes to give dibenzothiophenes in good yield. The value of this Diels–Alder route to dibenzothiophenes is enhanced by the fact that the dienes (**6**) and (**7**) exhibit opposite regioselectivity with the commercially available alkyne, ethyl trimethylsilylpropynoate, the resulting trimethylsilyl substituted compounds being versatile intermediates for further transformation into a variety of dibenzothiophenes.

Experimental

For general points see ref. 5.

Ethyl 2-Formylbenzo[b]*thiophen-3-ylacetate* (**10a**).—Tin(IV) chloride (4.5 ml, 38.3 mmol) was added dropwise to a stirred solution of ethyl benzo[*b*]thiophen-3-ylacetate[14] (**8**) (4.21 g, 19.1 mmol) in dry dichloromethane (50 ml) at −10 °C under nitrogen. Dichloromethyl methyl ether (2.1 ml, 23.0 mmol) was added dropwise and the mixture allowed to warm to 0 °C. After being stirred overnight, the mixture was poured into dilute hydrochloric acid, and extracted with dichloromethane. The extracts were washed with water and brine, dried ($MgSO_4$), and evaporated. The residue was crystallised from dichloromethane–light petroleum to give the *title compound* (**10a**) (1.68 g, 35%), m.p. 95–99 °C (Found: C, 62.9; H, 4.8; S, 12.6. $C_{13}H_{12}O_3S$ requires C, 62.9; H, 4.9; S, 12.9%); ν_{max}(Nujol) 1 718 and 1 657 cm^{-1}; δ(270 MHz; $CDCl_3$) 10.33 (1 H, s), 7.98–7.94 (1 H, m), 7.91–7.87 (1 H, m), 7.56–7.46 (2 H, m), 4.25 (2 H, s), 4.17 (2 H, q, *J* 7 Hz), and 1.23 (3 H, t, *J* 7 Hz); *m/z* 248 (M^+, 66%), 220 (11), 206 (56), 202 (31), 175 (100), 161 (16), and 147 (70).

2-Formylbenzo[b]*thiophen-3-ylacetic Acid* (**11a**).—A mixture of the formyl ester (**10a**) (1.65 g, 6.67 mmol) and aqueous potassium hydroxide (2 M; 20 ml) in THF (18 ml) and methanol (2 ml) was stirred at room temperature for 3 h. The mixture was diluted with water (50 ml), extracted with ether, and the ether layer discarded. The aqueous layer was acidified, and extracted with ether. The ether extracts were washed with water and brine, dried ($MgSO_4$), and evaporated to give the *title compound* (**11a**) (1.34 g, 91%), m.p. 155–160 °C (Found: C, 60.0; H, 3.6; S, 14.8. $C_{11}H_8O_3S$ requires C, 60.0; H, 3.7; S, 14.6%); ν_{max}(Nujol) 1 718 and 1 624 cm^{-1}; δ(270 MHz; [$^2H_6$]acetone) 10.42 (1 H, s), 8.09 (1 H, dd, *J*, 7, 1 Hz), 8.03 (1 H, dd, *J* 7, 1 Hz), 7.61–7.49 (2 H, m), and 4.45 (2 H, s); *m/z* 220 (M^+, 10%), 202 (4), 176 (100), 175 (74), and 147 (75).

Benzothieno[2,3-c]*pyran-3-one* (**6a**).—A solution of the formyl acid (**11a**) (69 mg, 0.31 mmol) in acetic anhydride (15 ml) was heated under reflux for 3 h. The mixture was concentrated under reduced pressure, and the residue chromatographed to

give the *title compound* (**6a**) (34 mg, 54%), m.p. 150–160 °C (decomp.) (Found: C, 65.3; H, 3.25; S, 15.6. $C_{11}H_6O_2S$ requires C, 65.3; H, 3.0; S, 15.85%); ν_{max}(Nujol) 3 057 and 1 691 cm^{-1}; λ_{max}(EtOH) 220 (ε 18 400), 238 (17 380), 290 (5 790), and 425 nm (2 930); δ(270 MHz; $CDCl_3$) 7.91 (1 H, d, *J* 7 Hz), 7.84 (1 H, d, *J* 1.2 Hz), 7.61–7.53 (2 H, m), 7.41–7.35 (1 H, m), and 6.78 (1 H, d, *J* 1.5 Hz); *m/z* 202 (M^+, 100%), 174 (54), 146 (44), and 102 (23).

Ethyl 2-Acetylbenzo[b]*thiophen-3-ylacetate* (**10b**).—Acetyl chloride (240 mg, 3.0 mmol) was added to a stirred solution of ethyl benzo[*b*]thiophen-3-ylacetate (**8**) (220 mg, 1.0 mmol) in dry dichloromethane (25 ml) at 0 °C under nitrogen. Tin(IV) chloride (1M; 6 ml) in dichloromethane was added dropwise and the mixture allowed to warm to room temperature. After being stirred for 48 h, water (25 ml) was added to the mixture which was then stirred for a further 30 min. More water (50 ml) was added, and the dichloromethane layer was separated, washed with brine, dried ($MgSO_4$), and evaporated. The residue was crystallised form ether–light petroleum to give the *title compound* (**10b**) (113 mg, 43%), m.p. 98–99 °C (Found: C, 63.8; H, 5.3; S, 12.0. $C_{14}H_{14}O_3S$ requires C, 64.1; H, 5.4; S, 12.2%); ν_{max}(CCl_4) 1 741 and 1 678 cm^{-1}; δ(270 MHz; $CDCl_3$) 7.85 (2 H, m), 7.48 (2 H, m), 4.35 (2 H, s), 4.16 (2 H, q, *J* 8 Hz), 2.64 (3 H, s), and 1.24 (3 H, t, *J* 8 Hz); *m/z* 262 (M^+, 47%), 218 (32), 216 (100), 189 (84), 188 (87), 175 (19), 147 (44), 128 (16), 115 (14), and 102 (19).

2-Acetylbenzo[b]*thiophen-3-ylacetic Acid* (**11b**).—A mixture of the ester (**10**) (50 mg, 0.19 mmol) and aqueous potassium hydroxide (2M; 5 ml) in THF (9 ml) and methanol (1 ml) was stirred at room temperature for 3 h. The mixture was diluted with water (30 ml) and extracted with ether (25 ml). The ether extract was discarded and the water layer acidified to pH1 and extracted with ether (3 × 25 ml). The ether extracts were washed with water and brine, dried ($MgSO_4$), and evaporated to give the *title compound* (**11b**) (36 mg, 81%), m.p. 220–224 °C (Found: M^+, 234.0346. $C_{12}H_{10}O_3S$ requires *M*, 234.0351); ν_{max}(Nujol) 1 711 and 1 666 cm^{-1}; δ(270 MHz; [$^2H_6$]acetone) 8.1 (2 H, m), 7.6 (2 H, m), 4.4 (2 H, s), and 2.62 (3 H, s); *m/z* 234 (M^+, 21%), 216 (13), 190 (75), 175 (100), 147 (48), and 43 (66).

1-Methylbenzothieno[2,3-c]*pyran-3-one* (**6b**).—*Method A.* The keto acid (**11b**) (20 mg, 0.09 mmol) was dissolved in acetic anhydride (5 ml) and the mixture heated under reflux for 12 h. It was then concentrated under reduced pressure and the residue dissolved in ethyl acetate. This solution was washed with aqueous sodium hydrogen carbonate and brine, dried ($MgSO_4$), and evaporated to give the *title compound* (**6b**) (12 mg, 65%), identical with the sample prepared by method B (see below).

Method B. Freshly distilled boron trifluoride–diethyl ether (1 ml) was added dropwise to a stirred solution of benzo[*b*]thiophen-3-ylacetic acid[14] (**9**) (710 mg, 3.7 mmol) in acetic anhydride (1 ml). The mixture was stirred at room temperature for 3 h, before being diluted with ether (25 ml). The resulting yellow precipitate was filtered off, washed with ether, water, and ether again, and dried *in vacuo* to give the *title compound* (**6b**) (530 mg, 66%), m.p. 225–226 °C (Found: C, 66.6; H, 3.7; S, 14.1. $C_{12}H_8O_2S$ requires C, 66.65; H, 3.7; S, 14.8%; ν_{max}(Nujol) 1 712 cm^{-1}; λ_{max}(EtOH) 221 (ε 12 510), 236 (12 460), 291 (3 250), 316 (2 150), 409 (4 950), and 430 nm (5 310); δ(270 MHz; [$^2H_6$]acetone) 8.16 (1 H, d, *J* 7.5 Hz), 7.80 (1 H, d, *J* 7.5 Hz), 7.65 (1 H, t, *J* 7.5 Hz), 7.45 (1 H, t, *J* 7.5 Hz), 6.75 (1 H, s), and 2.42 (3 H, s); *m/z* 216 (M^+, 100%), 201 (3), 188 (75), 173 (4), 160 (21), 145 (26), and 115 (15).

1-Pentylbenzothieno[2,3-c]*pyran-3-one* (**6c**).—Freshly distilled boron trifluoride–diethyl ether (1 ml) was added dropwise to a stirred solution of benzo[*b*]thiophen-3-ylacetic acid (**9**) (650 mg, 3.4 mmol) in hexanoic anhydride (2 ml) at 0 °C. The mixture was warmed to room temperature and stirred for 4 h. Water (20 ml) and pyridine (1 ml) were added and the mixture stirred for 15 min; it was then extracted with ether (3 × 25 ml). The combined ether extracts were washed with aqueous sodium hydrogen carbonate and brine and dried ($MgSO_4$). The ether was evaporated and the residue purified by chromatography to give the *title compound* (**6c**) (330 mg, 36%), m.p. 89–90 °C (Found: C, 70.4; H, 5.9; S, 11.5. $C_{16}H_{16}O_2S$ requires C, 70.6; H, 5.9; S, 11.8); ν_{max}($CHCl_3$) 1 707 cm^{-1}; λ_{max}(EtOH) 221 (ε 16 240), 240 (18 920), 290 (6 820), 410 (4 390), and 432 nm (4 720); δ(270 MHz; $CDCl_3$) 7.89 (1 H, m), 7.63–7.52 (2 H, m), 7.37 (1 H, m), 6.63 (1 H, s), 2.69 (2 H, t, *J* 7.6 Hz), 1.82 (2 H, m), 1.35 (4 H, m), and 0.90 (3 H, m); *m/z* 272 (M^+, 94%), 244 (16), 216 (17), 201 (29), 187 (100), 173 (14), 145 (62), and 115 (22).

Diels–Alder Reactions of Benzothieno[2,3-c]*pyran-3-one* (**6a**). —*With dimethyl acetylenedicarboxylate.* A mixture of the pyranone (**6a**) (59 mg, 0.29 mmol) and dimethyl acetylenedicarboxylate (83 mg, 0.58 mmol) in bromobenzene (10 ml) was heated under reflux for 5 h. The solvent was evaporated, and the residue was chromatographed to give *dimethyl dibenzothiophene-2,3-dicarboxylate* (**12a**) (69 mg, 79%), m.p. 102–104 °C (Found: C, 64.0; H, 3.9; S, 10.6. $C_{16}H_{12}O_4S$ requires C, 64.0; H, 4.0; S, 10.7%); ν_{max}(Nujol) 1 736 and 1 719 cm^{-1}; δ(270MHz; $CDCl_3$) 8.53 (1 H, s), 8.22 (2 H, m), 7.90 (1 H, m), 7.54 (2 H, m), 3.98 (3 H, s), and 3.97 (3 H, s); *m/z* 300 (M^+, 81%), 269 (100), and 149 (66).

With ethyl propiolate. A mixture of the pyranone (**6a**) (23 mg, 0.11 mmol) and ethyl propiolate (56 mg, 0.57 mmol) in bromobenzene (10 ml) was heated under reflux for 36 h. The solvent was evaporated and the residue chromatographed to give a mixture of *ethyl dibenzothiophene-2-carboxylate* (**12b**) and *ethyl dibenzothiophene-3-carboxylate* (**13b**) (19 mg, 65%) in the ratio 1:1 (Found: C, 70.2; H, 4.5; S, 12.2. $C_{15}H_{12}O_2S$ requires C, 70.3; H, 4.7; S, 12.5); ν_{max}(Nujol) 1 716 cm^{-1}; δ(270 MHz; $CDCl_3$) 8.85 (1 H, d, *J* 1.7 Hz, 3-isomer), 8.57 (1 H, s, 2-isomer), 8.27–8.11 (m), 7.91–7.85 (m), 7.55–7.49 (m), 4.46 (2 H, q, *J* 7 Hz), 4.44 (2 H, q, *J* 7 Hz), 1.46 (3 H, t, *J* 7 Hz), and 1.45 (3 H, t, *J* 7 Hz); *m/z* 256 (M^+, 100%), 228 (19), 211 (82), 183 (38), and 139 (26).

With ethyl trimethylsilylpropynoate. A mixture of the pyranone (**6a**) (26 mg, 0.13 mmol) and ethyl trimethylsilylpropynoate (44 mg, 0.26 mmol) in bromobenzene (10 ml) was heated under reflux for 36 h. The solvent was evaporated and the residue chromatographed to give a mixture of ethyl 3-trimethylsilyldibenzothiophene-2-carboxylate (**12c**) and ethyl 2-trimethylsilyldibenzothiophene-3-carboxylate (**13c**) (29 mg, 69%) in the ratio 6:1. Recrystallisation from dichloromethane–light petroleum gave pure *ethyl 3-trimethylsilyldibenzothiophene-2-carboxylate* (**12c**), m.p. 151–154 °C (Found: C, 65.8; H, 5.9; S, 10.0. $C_{18}H_{20}O_2SSi$ requires C, 65.8; H, 6.1; S, 9.8%); ν_{max}(Nujol) 1 708 cm^{-1}; δ(270 MHz; $CDCl_3$) 8.57 (1 H, s), 8.46 (1 H, s), 8.23 (1 H, m), 7.89 (1 H, m), 7.53–7.49 (2 H, m), 4.43 (2 H, q, *J* 7 Hz), 1.45 (3 H t, *J* 7 Hz), and 0.43 (9 H, s); *m/z* 328 (M^+, 5%), 313 (92), 285 (100), and 269 (14).

Diels–Alder Reactions of 1-Methylbenzothieno[2,3-c]*pyran-3-one* (**6b**).—*With dimethyl acetylenedicarboxylate.* A mixture of the pyranone (**6b**) (130 mg, 0.6 mmol) and dimethyl acetylenedicarboxylate (170 mg, 1.2 mmol) in bromobenzene (20 ml) was heated under reflux for 8 h. The solvent was evaporated and the residue was chromatographed to give *dimethyl 1-methyldibenzothiophene-2,3-dicarboxylate* (**12d**) (176 mg, 93%), m.p. 147 °C (Found: C, 64.7; H, 4.4; S, 10.0. $C_{17}H_{14}O_4S$ requires C, 64.95; H, 4.5; S, 10.2%); ν_{max}(Nujol) 1 725 cm^{-1}; δ(270 MHz; $CDCl_3$) 8.65 (1 H, s), 8.25–8.19 (1 H, m), 7.93–7.85 (1 H, m), 7.57–7.48 (2 H, m), 4.03 (3 H, s), 3.97 (3 H, s), and 2.57 (3 H, s);

m/z 314 (M^+, 98%), 283 (100), 282 (99), 267 (17), 255 (5), 240 (10), 224 (86), and 196 (39).

With ethyl propiolate. A mixture of the pyranone (**6b**) (110 mg, 0.5 mmol) and ethyl propiolate (250 mg, 2.5 mmol) in bromobenzene (20 ml) was heated under reflux for 24 h. The solvent was evaporated, and the residue chromatographed to give a mixture of *ethyl* 1-*methyldibenzothiophene*-2-*carboxylate* (**12e**) and *ethyl* 1-*methyldibenzothiophene*-3-*carboxylate* (**13e**) (109 mg, 79%) in the ratio 1.5:1, m.p. 47–53 °C (Found: M^+, 270.0713. $C_{16}H_{14}O_2S$ requires *M*, 270.0714); ν_{max}(Nujol) 1 715 cm^{-1}; δ(270 MHz; $CDCl_3$) 8.66 (1 H, s, minor), 8.23–8.18 (1 H, m, minor), 8.16–8.11 (1 H, m, major), 8.05–7.85 (m), 7.55–7.40 (m), 4.46 (2 H, q, *J* 7 Hz, minor), 4.43 (2 H, q, *J* 7 Hz, major), 2.85 (3 H, s, major), 2.60 (3 H, s, minor), 1.47 (3 H, t, *J* 7 Hz, minor), and 1.44 (3 H, t, *J* 7 Hz, major); *m/z* 270 (M^+, 100%), 255 (4), 242 (15), 225 (71), and 197 (41).

With ethyl trimethylsilylpropynoate. A mixture of the pyranone (**6b**) (110 mg, 0.5 mmol) and ethyl trimethylsilylpropynoate (260 mg, 1.5 mmol) in bromobenzene (20 ml) was heated under reflux for 70 h. The solvent was evaporated and the residue chromatographed to give, after recrystallisation from hexane, *ethyl* 1-*methyl*-3-*trimethylsilyldibenzothiophene*-2-*carboxylate* (**12f**) (117 mg, 67%), m.p. 101–103 °C (Found: C, 66.5; H, 6.45; S, 9.1. $C_{19}H_{22}O_2SSi$ requires C, 66.6; H, 6.5; S, 9.4%); ν_{max}(Nujol) 1 714 and 846 cm^{-1}; δ(270 MHz; $CDCl_3$) ~8.23 (1 H, s), 8.22–8.17 (1 H, m), 7.92–7.86 (1 H, m), 7.52–7.46 (2 H, m), 4.45 (2 H, q, *J* 7.5 Hz), 2.62 (3 H, s), 1.44 (3 H, t, *J* 7.5 Hz), and 0.38 (9 H, s); *m/z* 342 (M^+, 5%), 327 (99), 299 (100), 283 (11), 253 (5), 239 (6), 225 (10), 211 (10), 197 (6), 155 (9), and 149 (8).

Protodesilylation of the dibenzothiophene (**12f**). The dibenzothiophene (**12f**) (20 mg) was dissolved in a mixture of trifluoroacetic acid (2 ml) and water (1 ml), and heated to 70 °C for 2 h. The mixture was diluted with water (30 ml) and extracted with ether. The ether extracts were washed with aqueous sodium hydrogen carbonate, water, and brine, dried ($MgSO_4$), and evaporated to give *ethyl* 1-*methyldibenzothiophene*-2-*carboxylate* (**12e**) (12 mg, 76%), m.p. 74–79 °C (Found: M^+, 270.0718. $C_{16}H_{14}O_2S$ requires *M*, 270.015); ν_{max}(Nujol) 1 708 cm^{-1}; δ(270 MHz; $CDCl_3$) 8.18 (1 H, m), 8.02 (2 H, s), 7.90 (1 H, m), 7.50 (2 H, m), 4.43 (2 H, q, *J* 8 Hz), 2.87 (3 H, s), and 1.44 (3 H, t, *J* 8 Hz); *m/z* 270 (M^+, 100%), 241 (16), 225 (51), 224 (23), 197 (30), and 196 (13).

With methyl 4-*hydroxypent*-2-*ynoate.* A mixture of the pyranone (**6b**) (120 mg, 0.55 mmol) and methyl 4-hydroxypent-2-ynoate (140 mg, 1.10 mmol) in bromobenzene (20 ml) was heated under reflux for 80 h. The solvent was evaporated and the residue chromatographed to give 1,4-*dimethylfuro*[3,4-b]*dibenzothiophene*-3-*one* (**14a**) (68 mg, 46%), m.p. 229–231 °C (Found: M^+, 268.0557. $C_{16}H_{12}O_2S$ requires *M*, 268.0558); ν_{max}(Nujol) 1 750 cm^{-1}; δ(270 MHz; $CDCl_3$) 8.22 (1 H, d, *J* 8 Hz), 7.98 (1 H, s), 7.93 (1 H, d, *J* 8 Hz), 7.60–7.47 (2 H, m), 5.63 (1 H, q, *J* 7 Hz), 2.96 (3 H, s), and 1.67 (3 H, d, *J* 7 Hz); *m/z* 268 (M^+, 70%), 253 (60), 225 (100), and 197 (25).

With methyl tetrolate. A mixture of the pyranone (**6b**) (90 mg, 0.42 mmol) and methyl tetrolate (163 mg, 1.67 mmol) in bromobenzene (15 ml) was heated under reflux for 7 days. The solvent was evaporated, and the residue chromatographed to give a mixture of *methyl* 1,3-*dimethyldibenzothiophene*-2-*carboxylate* (**12h**) and *methyl* 1,2-*dimethyldibenzothiophene*-3-*carboxylate* (**13h**) (66 mg, 59%) in the ratio 5:1, m.p. 80–83 °C (Found: C, 70.8; H, 5.15. $C_{16}H_{14}O_2S$ requires C, 71.1; H, 5.2%); ν_{max}(Nujol) 1 720 cm^{-1}; δ(270 MHz; $CDCl_3$) 8.49 (1 H, s, minor), 8.12 (m), 7.87 (m), 7.85 (1 H, s, major), 7.45 (m), 3.98 (3 H, s, major), 3.97 (3 H, s, minor), 2.64 (3 H, s, minor), 2.57 (3 H, s, minor), 2.55 (3 H, s, major), and 2.50 (3 H, s, major); *m/z* 270 (M^+, 100%), 239 (36), 238 (20), 211 (22), and 210 (27).

With methyl phenylpropiolate. A mixture of the pyranone (**6b**) (98 mg, 0.45 mmol) and methyl phenylpropiolate (180 mg, 1.13 mmol) in bromobenzene (15 ml) was heated under reflux for 6 days. The solvent was evaporated, and the residue chromatographed to give (i) *methyl* 1-*methyl*-3-*phenyldibenzothiophene*-2-*carboxylate* (**12i**) (57 mg, 38%), m.p. 124–126 °C (Found: C, 75.7; H, 4.8. $C_{21}H_{16}O_2S$ requires C, 75.9; H, 4.85%); ν_{max}(Nujol) 1 723 and 1 259 cm^{-1}; δ(270 MHz; $CDCl_3$) 8.15 (1 H, d, *J* 7 Hz), 8.01 (1 H, s), 7.90 (1 H, d, *J* 7.5 Hz), 7.51–7.38 (7 H, m), 3.62 (3 H, s), and 2.64 (3 H, s); *m/z* 332 (M^+, 100%), 301 (37), 286 (6), 271 (19), and 258 (14); and (ii) *methyl* 1-*methyl*-2-*phenyldibenzothiophene*-3-*carboxylate* (**13i**) (49 mg, 33%), m.p. 129–131 °C (Found: C, 75.7; H, 5.0. $C_{21}H_{16}O_2S$ requires C, 75.9; H, 4.85%); ν_{max}(Nujol) 1 727 cm^{-1}; δ(270 MHz; $CDCl_3$) 8.56 (1 H, s), 8.21 (1 H, m), 7.90 (1 H, m), 7.53–7.38 (6 H, m), 7.23 (1 H, m), 3.61 (3 H, s), and 2.34 (3 H, s); *m/z* 332 (M^+, 100%), 301 (36), 286 (7), 271 (20), and 258 (11).

With benzyne. A mixture of the pyranone (**6b**) (76 mg, 0.35 mmol) and 2-(3,3-dimethyltriazen-1-yl)benzoic acid (136 mg, 0.70 mmol) in bromobenzene (15 ml) was heated under reflux for 12 h. The solvent was evaporated and the residue chromatographed to give, after recrystallisation from dichloromethane–light petroleum, 6-*methylbenzo*[b]*dibenzothiophene* (**15**) (34 mg, 39%), m.p. 98–101 °C (Found: C, 82.35; H, 4.8. $C_{17}H_{12}S$ requires C, 82.2; H, 4.9%); ν_{max}(Nujol) 3 067, 1 456, 1 381, 878, 756, and 724 cm^{-1}; δ(270 MHz; $CDCl_3$) 8.52 (1 H, s), 8.26 (1 H, m), 8.12 (1 H, d, *J* 8 Hz), 8.05 (1 H, d, *J* 8 Hz), 7.85 (1 H, m), 7.59–7.47 (4 H, m), and 2.92 (3 H, s); *m/z* 248 (M^+, 100%) and 247 (37).

Diels–Alder Reactions of 1-*Pentylbenzothieno*[2,3-c]*pyran*-3-*one* (**6c**).—*With dimethyl acetylenedicarboxylate.* A mixture of the pyranone (**6c**) (80 mg, 0.29 mmol) and dimethyl acetylenedicarboxylate (84 mg, 0.59 mmol) in bromobenzene (15 ml) was heated under reflux for 14 h. The solvent was evaporated and the residue was chromatographed to give *dimethyl* 1-*pentyldibenzothiophene*-2,3-*dicarboxylate* (**12j**) (74 mg, 68%), m.p. 60–61 °C (Found: C, 68.4; H, 5.9; S, 8.6. $C_{21}H_{22}O_4S$ requires C, 68.1; H, 6.0; S, 8.65); ν_{max}(CCl_4) 1 730 cm^{-1}; δ(270 MHz; $CDCl_3$) 8.66 (1 H, s), 8.20 (1 H, m), 7.90 (1 H, m), 7.55 (2 H, m), 4.02 (3 H, s), 3.98 (3 H, s), 2.91 (2 H, t, *J* 8.5 Hz), 1.80 (2 H, m), 1.40 (4 H, m), and 0.92 (3 H, t, *J* 6.5 Hz); *m/z* 370 (M^+, 51%), 339 (35), 338 (49), 295 (100), 147 (32), 111 (45), 71 (13), and 57 (30).

With ethyl propiolate. A mixture of the pyranone (**6c**) (80 mg, 0.29 mmol) and ethyl propiolate (144 mg, 1.47 mmol) in bromobenzene (20 ml) was heated under reflux for 36 h. The solvent was evaporated, and the residue chromatographed to give a mixture of *ethyl* 1-*pentyldibenzothiophene*-2-*carboxylate* (**12k**) and *ethyl* 1-*pentyldibenzothiophene*-3-*carboxylate* (**13k**) (52 mg, 54%) in the ratio 1:1 (Found: C, 73.3; H, 6.8; S, 9.9. $C_{20}H_{22}O_2S$ requires C, 73.6; H, 6.8; S, 9.8%); ν_{max}(film) 1 718 cm^{-1}; δ(270 MHz; $CDCl_3$) 8.70 (1 H, d, *J* 2 Hz), 8.23 (1 H, m), 8.15 (1 H, m), 8.00 (2 H, s), 7.95 (1 H, d, *J* 2 Hz), 7.55–7.45 (4 H, m), 4.5–4.4 (4 H, m), 3.25 (2 H, t, *J* 8 Hz, 2-ester), 2.93 (2 H,t, *J* 8 Hz, 3-ester), 1.90–1.75 (4 H, m), 1.60–1.40 (14 H, m), and 1.0–0.9 (6 H, m); *m/z* 326 (M^+, 100%), 281 (23), 269 (24), 241 (42), and 197 (43).

With ethyl trimethylsilylpropynoate. A mixture of the pyranone (**6c**) (40 mg, 0.15 mmol) and ethyl trimethylsilylpropynoate (50 mg, 0.29 mmol) in bromobenzene (10 ml) was heated under reflux for 7 days. The solvent was evaporated, and the residue chromatographed to give *ethyl* 1-*pentyl*-3-*trimethylsilyldibenzothiophene*-2-*carboxylate* (**12l**) (34 mg, 60%) as a yellow oil (Found: C, 69.4; H, 7.5; S, 8.1. $C_{23}H_{30}O_2SSi$ requires C, 69.3; H, 7.6; S, 8.0%); ν_{max}(film) 1 722 cm^{-1}; δ(270 MHz; $CDCl_3$) 8.23 (1 H, s), 8.20 (1 H, m), 7.90 (1 H, m), 7.45 (2 H, m), 4.42 (2 H, q, *J* 8 Hz), 2.92 (2 H, t, *J* 8 Hz), 1.80 (2 H, m), 1.40 (7 H, m), 0.94 (3 H, t, *J* 6 Hz), and 0.38 (9 H, s); *m/z* 398 (M^+, 8%), 383 (100), 355 (37), and 297 (16).

With methyl 4-hydroxypent-2-ynoate. A mixture of the pyranone (**6c**) (47 mg, 0.17 mmol) and methyl 4-hydroxypent-2-ynoate (44 mg, 0.35 mmol) in bromobenzene (10 ml) was heated under reflux for 8 days. The solvent was evaporated and the residue chromatographed to give *4-methyl-1-pentylfuro*[3,4-b]*dibenzothiophen-3-one* (**14b**) (31 mg, 55%), m.p. 138–139 °C (Found: C, 73.8; H, 6.1; S, 9.6. $C_{20}H_{20}O_2S$ requires C, 74.0; H, 6.2; S, 9.9%); ν_{max}(Nujol) 1 744 cm^{-1}; δ(270 MHz; $CDCl_3$) 8.18 (1 H, dd, *J* 8, 2 Hz), 7.93 (1 H, s), 7.88 (1 H, dd, *J* 8, 2 Hz), 7.50 (2 H, m), 5.62 (1 H, q, *J* 8 Hz), 3.38 (2 H, t, *J* 8 Hz), 1.80 (2 H, m), 1.72 (3 H, d, *J* 8 Hz), 1.40 (4 H, m), and 0.90 (3 H, t, *J* 7 Hz); *m/z* 324 (M^+, 100%), 281 (66), 268 (56), 267 (55), and 225 (33).

With methyl tetrolate. A mixture of the pyranone (**6c**) (62 mg, 0.29 mmol) and methyl tetrolate (89 mg, 0.91 mmol) in bromobenzene (10 ml) was heated under reflux for 11 days. The solvent was evaporated, and the residue chromatographed to give a mixture of *methyl 3-methyl-1-pentyldibenzothiophene-2-carboxylate* (**12n**) and *methyl 2-methyl-1-pentyldibenzothiophene-3-carboxylate* (**13n**) (25 mg, 34%) in the ratio 6:1 (Found: C, 73.8; H, 7.0. $C_{20}H_{22}O_2S$ requires C, 73.6; H, 6.8%); ν_{max}($CHCl_3$) 1 723 and 1 271 cm^{-1}; δ(270 MHz; $CDCl_3$) 8.48 (1 H, s, minor), 8.15–8.10 (m), 7.90–7.85 (m), 7.85 (1 H, s, major), 7.5–7.4 (m), 3.96 (s), 2.95 (2 H, m, minor), 2.85 (2 H, m, major), 2.64 (3 H, s, minor), 2.45 (3 H, s, major), 1.8–1.7 (m), 1.5–1.3 (m), and 1.0–0.9 (m); *m/z* 326 (M^+, 100%), 295 (15), 269 (39), and 251 (11).

With methyl phenylpropiolate. A mixture of the pyrone (**6c**) (60 mg, 0.22 mmol) and methyl phenylpropiolate (90 mg, 0.55 mmol) in bromobenzene (7 ml) was heated under reflux for 11 days. The solvent was evaporated, and the residue chromatographed to give a mixture of *methyl 1-pentyl-3-phenyldibenzothiophene-2-carboxylate* (**12o**) and *methyl 1-pentyl-2-phenyldibenzothiophene-3-carboxylate* (**13o**) (60 mg, 70%) in the ratio 1.6:1 (Found: C, 77.3; H, 6.3. $C_{25}H_{24}O_2S$ requires C, 77.3; H, 6.2%); ν_{max}($CHCl_3$) 1 723 and 1 262 cm^{-1}; δ(270 MHz; $CDCl_3$) 8.54 (1 H, s, minor), 8.21 (1 H, m, minor), 8.15 (1 H, m, major), 8.00 (1 H, s, major), 7.89 (m), 7.52–7.40 (m), 7.20 (1 H, m, minor), 3.594 (3 H, s, minor), 3.590 (3 H, s, major), 2.98 (2 H, m, major), 2.69 (2 H, m, minor), 1.90 (2 H, m, major), 1.40 (m), 1.20 (m), 0.93 (3 H, t, *J* 7 Hz, major), 0.80 (3 H, t, *J* 7 Hz, minor); *m/z* 388 (M^+, 100%), 357 (10), 331 (14), 299 (22), and 271 (27).

Ethyl 3-Formylbenzo[b]*thiophen-2-ylacetate* (**17a**).—Tin(IV) chloride (1.3 ml, 11.3 mmol) was added dropwise to a stirred solution of ethyl benzo[*b*]thiophen-2-ylacetate (**16a**) (831 mg, 3.77 mmol) in dry dichloromethane (10 ml) at −20 °C under nitrogen. Dichloromethyl methyl ether (0.41 ml, 4.52 mmol) was added dropwise and the mixture allowed to warm to 0 °C. After the mixture had been stirred overnight, it was poured into dilute hydrochloric acid, and extracted with dichloromethane. The extracts were washed with water and brine, dried ($MgSO_4$), and evaporated. The residue was chromatographed to give the *title compound* (**17a**) (713 mg, 76%) as a yellow oil (Found: C, 63.0; H, 4.85; S, 12.8. $C_{13}H_{12}O_3S$ requires C, 62.9; H, 4.9; S, 12.9%); ν_{max}(film) 3 061, 2 763, 1 739, and 1 672 cm^{-1}; δ(270 MHz; $CDCl_3$) 10.39 (1 H, s), 8.54 (1 H, d, *J* 8 Hz), 7.82 (1 H, d, *J* 7.5 Hz), 7.52–7.39 (2 H, m), 4.31 (2 H, s), 4.23 (2 H, q, *J* 7 Hz), and 1.29 (3 H, t, *J* 7 Hz); *m/z* 248 (M^+, 72%), 220 (4), 206 (68), 202 (59), 191 (15), 175 (100), and 147 (82).

Benzothieno[3,2-c]*pyran-3-one* (**7a**).—A mixture of the formyl ester (**17a**) (421 mg, 1.70 mmol) and potassium hydroxide solution (2M; 4 ml) in THF (9 ml) and methanol (1 ml) was stirred at room temperature for 3 h. The mixture was diluted with water (10 ml), extracted with ether, and the ether layer discarded. The aqueous layer was acidified and extracted with ether. The ether extracts were washed with water and brine, dried ($MgSO_4$), and evaporated to give 3-formylbenzo[*b*]-thiophen-2-ylacetic acid (**18a**). The crude acid was dissolved in acetic anhydride (30 ml) and the solution heated under reflux for 3 h. It was then concentrated under reduced pressure and the residue purified by chromatography to give the *title compound* (**7a**) (145 mg, 42%), m.p. 165 °C (decomp.) (Found: M^+, 202.0087. $C_{11}H_6O_2S$ requires *M*, 202.0089; ν_{max}(Nujol) 3 062, 1 703, 1 635, and 1 536 cm^{-1}; λ_{max}(EtOH) 220 (ε 19 560), 232 (20 900), 255 (11 650), 266 (13 380), 272 (14 080), and 278 nm (11 420); δ(270 MHz; $CDCl_3$) 8.26 (1 H, d, *J* 1.5 Hz), 7.70 (1 H, m), 7.55 (1 H, m), 7.44–7.36 (2 H, m), and 6.52 (1 H, d, *J* 1.2 Hz); *m/z* 202 (M^+, 100%), 174 (49), 146 (42), 145 (36), and 102 (22).

Ethyl 3-Acetylbenzo[b]*thiophen-2-ylacetate* (**17b**).—A solution of ethyl benzo[*b*]thiophen-2-ylacetate (**16a**) (415 mg, 1.88 mmol) in dry dichloromethane (5 ml) was added dropwise to a stirred mixture in tin(IV) chloride (0.65 ml, 5.6 mmol) and acetyl chloride (0.16 ml, 2.3 mmol) in dry dichloromethane (10 ml) under nitrogen. The mixture was stirred overnight at room temperature, diluted with water (20 ml), and extracted with dichloromethane. The dichloromethane extract was washed with water and brine, dried ($MgSO_4$), and evaporated, and the residue chromatographed to give the *title compound* (**17b**) (228 mg, 46%) as a yellow oil (Found: C, 64.0; H, 5.4. $C_{14}H_{14}O_3S$ requires C, 64.1; H, 5.4%); ν_{max}(film) 1 739 and 1 669 cm^{-1}; δ(270 MHz; $CDCl_3$) 8.03 (1 H, d, *J* 8 Hz), 7.81 (1 H, d, *J* 8 Hz), 7.45–7.37 (2 H, m), 4.20 (2 H, q, *J* 7 Hz), 4.13 (2 H, s), 2.70 (3 H, s), and 1.28 (3 H, t, *J* 7 Hz); *m/z* 262 (M^+, 84%), 216 (100), and 188 (71).

1-Methylbenzothieno[3,2-c]*pyran-3-one* (**7b**).—Freshly distilled boron trifluoride–diethyl ether (0.25 ml) was added dropwise to a stirred solution of benzo[*b*]thiophen-2-ylacetic acid[16] (**16b**) (221 mg, 1.15 mmol) in acetic anhydride (0.5 ml). The mixture was stirred at room temperature for 3 h before being diluted with ether (20 ml). The precipitate was filtered off, washed with ether, sodium hydrogen carbonate solution, water, and ether again, and dried *in vacuo* to give the *title compound* (**7b**) (143 mg, 58%), m.p. 160–164 °C (Found: M^+, 216.0239. $C_{12}H_8O_2S$ requires *M*, 216.0245); ν_{max}(Nujol) 1 708 cm^{-1}; λ_{max}(EtOH) 219 (ε 52 390), 234 (78 690), 266 (64 690), 273 (70 450), 307 (10 320), 319 10 860), and 364 nm (11 040); δ(270 MHz; [$^2H_6$]acetone) 7.90 (1 H, m), 7.72 (1 H, m), 7.44 (2 H, m), 6.44 (1 H, d, *J* 0.7 Hz), and 2.78 (3 H, s); *m/z* 216 (M^+, 100%), 201 (11), 188 (80), and 145 (35).

Diels–Alder Reactions of Benzothieno[3,2-c]*pyran-3-one* (**7a**). —*With dimethyl acetylenedicarboxylate.* A mixture of the pyranone (**7a**) (12 mg, 0.06 mmol) and dimethyl acetylenedicarboxylate (17 mg, 0.12 mmol) in bromobenzene (5 ml) was heated under reflux for 7 h. The solvent was evaporated and the residue was chromatographed to give dimethyl dibenzothiophene-2,3-dicarboxylate (**19a**) = (**12a**) (13 mg, 73%), identical with the previous sample.

With ethyl propiolate. A mixture of the pyranone (**7a**) (51 mg, 0.25 mmol) and ethyl propiolate (124 mg, 1.26 mmol) in bromobenzene (10 ml) was heated under reflux for 24 h. The solvent was evaporated and the residue chromatographed to give a mixture of *ethyl dibenzothiophene-2-carboxylate* (**19b**) = (**12b**) and *ethyl dibenzothiophene-3-carboxylate* (**20b**) = (**13b**) (48 mg, 74%) in the ratio 1:1.6, m.p. 43–59 °C, data given previously.

With ethyl trimethylsilylpropynoate. A mixture of the pyranone (**7a**) (69 mg, 0.34 mmol) and ethyl trimethylsilylpropynoate (174 mg, 1.02 mmol) in bromobenzene (15 ml) was heated under reflux for 24 h. The solvent was evaporated and the residue chromatographed to give a mixture of ethyl 3-trimethylsilyldibenzothiophene-2-carboxylate (**19c**) = (**12c**) and ethyl 2-trimethylsilyldibenzothiophene-3-carboxylate (**20c**) = (**13c**) in the ratio 1:10, m.p. 85–87 °C (Found: C, 65.7; H, 6.1; S, 9.6.

$C_{18}H_{20}O_2SSi$ requires C, 65.8; H, 6.1; S, 9.8%); ν_{max}(Nujol) 1 713, 1 248, 843, and 761 cm^{-1}; δ(270 MHz; $CDCl_3$) [data for (**20c**) only] 8.82 (1 H, s), 8.23 (1 H, m), 8.17 (1 H, s), 7.87 (1 H, m), 7.51–7.48 (2 H, m), 4.47 (2 H, q, *J* 7 Hz), 1.49 (3 H, t, *J* 7 Hz), and 0.44 (9 H, s); *m/z* 328 (M^+, 11%), 313 (100), and 285 (94).

Diels–Alder Reactions of 1-*Methylbenzothieno*[3,2-c]*pyran*-3-*one* (**7b**).—*With dimethyl acetylenedicarboxylate.* A mixture of the pyranone (**7b**) (183 mg, 0.85 mmol) and dimethyl acetylenedicarboxylate (241 mg, 1.69 mmol) in bromobenzene (25 ml) was heated under reflux for 9 h. The solvent was evaporated and the residue was chromatographed to give *dimethyl* 4-*methyldibenzothiophene*-2,3-*dicarboxylate* (**19d**) (195 mg, 73%), m.p. 153 °C (Found: C, 64.7; H, 4.4; S, 10.3. $C_{17}H_{14}O_4S$ requires C, 64.95; H, 4.5; S, 10.2%); ν_{max}(Nujol) 1 729 and 1 714 cm^{-1}; δ(270 MHz; $CDCl_3$) 8.46 (1 H, m), 8.43 (1 H, s), 7.93 (1 H, m), 7.54 (2 H, m), 4.02 (3 H, s), 3.95 (3 H, s), and 2.89 (3 H, s) *m/z* 314 (M^+, 100%), 283 (87), 282 (86), 224 (73), and 196 (34).

With ethyl propiolate. A mixture of the pyranone (**7b**) (91 mg, 0.42 mmol) and ethyl propiolate (210 mg, 2.1 mmol) in bromobenzene (15 ml) was heated under reflux for 40 h. The solvent was evaporated and the residue chromatographed to give a mixture of *ethyl* 4-*methyldibenzothiophene*-2-*carboxylate* (**19e**) and *ethyl* 4-*methyldibenzothiophene*-3-*carboxylate* (**20e**) (86 mg, 76%) in the ratio 1:1.9, m.p. 53–58 °C (Found: C, 71.2; H, 5.1; S, 11.7. $C_{16}H_{14}O_2S$ requires C, 71.1; H, 5.2; S, 11.9%); ν_{max}(Nujol) 3 061 and 1 713 cm^{-1}; δ(270 MHz; $CDCl_3$) 8.51–8.45 (1 H, m, major), 8.44 (1 H, m, major), 7.94–7.88 (4 H, m, minor), 7.85 (1 H, d, *J* 8.5 Hz, major), 7.74 (1 H, dd, *J* 8, 0.5 Hz, major), 7.54–7.48 (m), 4.43 (2 H, q, *J* 7 Hz, both isomers), 3.14 (3 H, s, major), 2.97 (3 H, s, minor)), 1.45 (3 H, t, *J* 7 Hz, minor), and 1.44 (3 H, t, *J* 7 Hz, major); *m/z* 270 (M^+, 100%), 241 (12), 225 (59), 197 (36), and 149 (55).

With ethyl trimethylsilylpropynoate. A mixture of the pyranone (**7b**) (107 mg, 0.5 mmol) and ethyl trimethylsilylpropynoate (170 mg, 1 mmol) in bromobenzene (15 ml) was heated under reflux for 8 days. The solvent was evaporated, and the residue chromatographed to give, after recrystallisation from hexane, *ethyl* 4-*methyl*-2-*trimethylsilyldibenzothiophene*-3-*carboxylate* (**20f**) (52 mg, 31%), m.p. 97–99 °C (Found: C, 66.5; H, 6.5; S, 9.4. $C_{19}H_{22}O_2SSi$ requires C, 66.6; H, 6.5; S, 9.4%); ν_{max}(Nujol) 1 719, 1 256, 1 169, and 841 cm^{-1}; δ(270 MHz; $CDCl_3$) 8.39–8.42 (1 H, m), 7.94 (1 H, s), 7.92–7.89 (1 H, m), 7.52–7.47 (2 H, m), 4.45 (2 H, q, *J* 7 Hz), 2.89 (3 H, s), 1.45 (3 H, t, *J* 7 Hz), and 0.36 (9 H, s); *m/z* 342 (M^+, 14%), 327 (100), 299 (98), and 283 (8).

With methyl tetrolate. A mixture of the pyranone (**7b**) (52 mg, 0.24 mmol) and methyl tetrolate (94 mg, 0.96 mmol) in bromobenzene (5 ml) was heated under reflux for 8 days. The solvent was evaporated, and the residue chromatographed to give a mixture of methyl 3,4-dimethyldibenzothiophene-2-carboxylate (**19g**) and methyl 2,4-dimethyldibenzothiophene-3-carboxylate (**20g**) (23 mg, 35%) in the ratio 1:10. Recrystallisation from dichloromethane–light petroleum gave pure *methyl* 2,4-*dimethyldibenzothiophene*-3-*carboxylate* (**20g**), m.p. 120–123 °C (Found: C, 71.15; H, 5.5. $C_{16}H_{14}O_2S$ requires C, 71.1; H, 5.2%); ν_{max}($CHCl_3$) 1 724 cm^{-1}; δ(270 MHz; $CDCl_3$) 8.35 (1 H, m), 7.87 (1 H, m), 7.58 (1 H, s), 7.45 (2 H, m), 3.99 (3 H, s), 2.84 (3 H, s), and 2.44 (3 H, s); *m/z* 270 (M^+, 100%), 255 (3), 239 (54), 238 (25), 211 (22), and 210 (23).

With methyl phenylpropiolate. A mixture of the pyranone (**7b**) (51 mg, 0.24 mmol) and methyl phenylpropiolate (94 mg, 0.59 mmol) in bromobenzene (5 ml) was heated under reflux for 8 days. The solvent was evaporated, and the residue chromatographed to give a mixture of *methyl* 4-*methyl*-3-*phenyldibenzothiophene*-2-*carboxylate* (**19h**) and *methyl* 4-*methyl*-2-*phenyldibenzothiophene*-3-*carboxylate* (**20h**) (52 mg, 66%) in the ratio 1:3, m.p. 136–149 °C (Found: C, 75.6; H, 4.85. $C_{21}H_{16}O_2S$ requires C, 75.9; H, 4.85%); ν_{max}($CHCl_3$) 1 724 cm^{-1}; δ(270 MHz; $CDCl_3$) 8.45 (m), 8.24 (1 H, s, minor), 7.90 (m), 7.75 (1 H, s, major), 7.52–7.39 (m), 3.63 (3 H, s, major), 3.58 (3 H, s, minor), 2.94 (3 H, s, major), and 2.67 (3 H, s, minor); *m/z* 332 (M^+, 100%), 301 (39), 286 (8), 271 (23), 258 (14), and 239 (3).

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